Patent claims

1. Process for the preparation of nitrodiphenylamines comprising reacting nitrohalogenobenzenes with anilines, a base and a catalyst of the formula

$$\begin{bmatrix} M-N & X & M & \\ & & & \\ &$$

wherein

X is a 1,2-ethanediyl or 1,2-ethenediyl radical and

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M can be identical or different and represents C₁-C₁₉-alkyl, C₇-C₁₉-aralkyl, C₆-C₁₈ aryl groups or C₆-C₁₉-heteroaryls having 1 to 3 nitrogen atoms, wherein two or more radicals M can be bridged in any desired manner by a covalent bridge or by an alkylidene bridge containing 1 to 4 carbon atoms or via an aryl or heteroaryl ring,

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Y represents halogen or a trifluoroacetyl, trifluoromethanesulfonyl, nonafluorobutanesulfonyl, cyanide, acetyl, fluorinated acetylacetonyl, nitrate, arylsulfonyl, oxinate, phosphate, carbonate or tetrafluoroborate radical,

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z represents 1, 2 or 3,

- m represents integers from 1 to 6 and
- r denotes 0, 1 or 2.
- Process according to Claim 1, wherein the base is chosen from the group consisting of bicarbonates, carbonates, methanolates, ethanolates, isopropylates, tert-butanolates, phosphates, fluorides, silazanes, hydrides and acetates of lithium, sodium, potassium and caesium.
- Process according to Claim 1, wherein the catalyst is prepared by deprotonation ligands of the formula (II)

with a base and subsequently reacting with a copper compound of the formula (III)

15 Cu-Y_{r} (III)

wherein M, X, Y, z and r defined the same as in formula (I), and wherein "An" is an anion of an acid havig a pKa value of 3 or less.

- 4. Process according to Claim 3, wherein the catalyst of the formula:(I) is prepared in situ.
- 5. Process according to Claim 1, wherein the catalyst is selected from the group consisting of (N,N'-dimethylimidazolidene)-copper(II) bromide, (N,N'-dicyclohexylimidazolidene)-copper[II] bromide, [N,N'-di(2,4,6-trimethyl)phenylimidazolidene]-copper(II) bromide, [N,N'-di(2-pyridyl)imidazolidene]-copper[II] bromide, (N-benzyl-N'-methyl-imidazolidene)-copper[II] bromide, {1,3-bis-[N-(N'-methyl)imidazolidene-methyl]-5-methylbenzene}-copper[II] bromide, {1,3-bis-[N-(N'-methyl)imidazolidene-methyl]-5-methylbenzene-methylb

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methyl)imidazolidene-methyl]-5-methylbenzene}-copper[I] trifluoromethylsulfonate, {2,6-bis-[N-(N'-methyl)-imidazolidene-methyl]pyridine}-copper[II] bromide, {1,2-bis-[N-(N'-methyl)imidazolidene]-1,2-diphenylethane}-copper[II] bromide and {bis-[N-(N'-methyl)imidazolidene]methane}-copper[II] bromide. (N,N'-Dimethyl-imidazolidene)-copper(II) bromide and {1,3-[bis-(N-(N'-methyl)imidazolidenemethyl]-5-methylbenzene}-copper[II] bromide.

- 6. Process according to Claim 1, wherein the nitrohalogenated benzenes are selected from the group consisting of 4-nitro-2-methylchlorobenzene, 4-nitro-3-methylfluorobenzene, 4-nitrochlorobenzene, 3-nitro-chlorobenzene or 2-nitrochlorobenzene, 4-nitrochlorobenzene, 4-nitrophenyl-trifluoromethanesulfonic acid ester, 4-nitrophenylnonafluorobutanesulfonic acid ester, 4-nitrophenyl carbamate and 4-nitrophenyltrifluoromethylsulfonic acid ester.
 - 7. The process according to Claim 1, wherein the aniline is a o-, m- or p-substituted aniline.
- The process according to Claim 7, wherein the substituted aniline is selected from the group consisting of vinylaniline, 4-tert.-butylaniline, p-anisidine, o-anisidine, o-toluidine, p-toluidine, anthranilic acid methyl ester, o-aminobenzonitrile, p-aminobenzonitrile and 4-ethylaniline.
- 25 9. Process for the preparation of aminodiphenylamine, wherein the nitrodiphenylamine produced according to Claim 1 is hydrogenated without isolation.